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PATENT SPECIFICATION

857,798

NO DRAWINGS.

Inventor :—JAMES DONALD BURNETT.

Date of filing Complete Specification : April 3, 1959.

Application Date : April 18, 1958. No. 12339/58.

Complete Specification Published : Jan. 4, 1961.

Index at Acceptance :—**Class 2(6),** P4(D1B : K8), P4T2(G : X), P7D(1A : 2A2B), P7T(1X : 2X), P12.

International Classification :—C08f.

COMPLETE SPECIFICATION.

Process for the Production of Polymeric Materials.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to a process for the production of polymeric materials.

When the process of this invention is used for the production of copolymers, the products obtained are characterised by the presence in the molecule of long homopolymeric segments. Such copolymers are known as segmented copolymers. They may be of the type known as graft copolymers which consist of molecules having a backbone or skeleton of a polymer of one variety and side chains or branches of a different polymer and thus have a structure of the type

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            B—B—B— . . . . .
            |
. . . . . —A—A—A—A—A—A— . . . . .
                      |
                      B—B—B— . . . . .
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where A represents the monomeric unit of the polymer making up the backbone or skeleton of the copolymer and B represents the monomeric unit making up the side chains or branches. They may also be of the type known as block copolymers which have a structure of the type

. . . . . —A—A—A—A—B—B—B—B— . . . .

Copolymers produced by the process of this invention may also have molecules in which both of these types of structure are present, i.e. they may be combinations of graft copolymers and block copolymers.

The process of this invention may also be used to modify the molecular structure of homopolymers. Thus a homopolymer having a substantially linear structure

. . . . . —A—A—A—A—A—A— . . . . .

may be converted into one having a branched structure of the type

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            A—A—A— . . . . .
            |
. . . . . —A—A—A—A—A—A— . . . . .
                      |
                      A—A—A— . . . . .
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In this way, it is possible to modify various properties, e.g. the solubility characteristics, of homopolymers.

In this Specification the expression segmented polymers is used as a generic term embracing both homopolymers having a branched structure of the type indicated above and also segmented copolymers.

According to the present invention we provide a process for the production of segmented polymers in which a normally solid high polymer having molecules containing peroxy groups is irradiated with ultra-violet light in the presence of a monomeric compound containing one or more olefinic double bonds and capable of polymerisation under the influence of free radicals, this irradiation being carried out in the absence of a concentration of oxygen which would otherwise inhibit polymerisation of said monomeric compound.

In our co-pending Application 12338/58 (Serial No. 857,797) we provide a process for the production of segmented polymers in

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which a normally solid thermoplastic high polymer is masticated in an oxygen-containing atmosphere at a temperature below 170° C. whereby peroxy groups are formed in the polymer, and is subsequently subjected to conditions causing the decomposition of peroxy groups in the presence of a monomeric compound containing one or more olefinic double bonds and capable of polymerisation under the influence of free radicals, this latter step being carried out in the absence of a concentration of oxygen which would otherwise inhibit polymerisation of the said monomeric compound.

The normally solid high polymer used in the process of this invention may be of synthetic or natural origin. If a synthetic polymer is used, it may be of either the addition or condensation type. Examples of addition-type polymers include polythene, polypropylene, polyisobutylene, polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyvinyl formal, polyvinyl butyral, poly N-vinyl pyrrolidone, polyvinyl pyridines, polyvinylidene chloride, polymethyl methacrylate, polybutyl methacrylate, polyacrylonitrile, polytrifluoromonochloroethylene, polytetrafluoroethylene, polybutadiene-1,3, polyisoprene and polychloroprene. Interpolymers and mixtures of polymers may also be used, e.g. interpolymers of butadiene 1,3 and styrene, acrylonitrile or methyl methacrylate. Examples of condensation-type polymers include epoxide polymers, polyethylene glycols, superpolyesters, superpolyamides, polyurethanes, polyureas and polysulphonamides. Examples of naturally occurring polymers include rubber, gutta percha, balata, cellulose, wool, cotton, silk, starch, casein, copal resins, shellac, and alginates. The invention is also applicable to modified naturally-occurring polymers e.g. to cellulose esters, ethers and acetals, cyclised natural rubber, rubber hydrochlorides and chlorinated rubber.

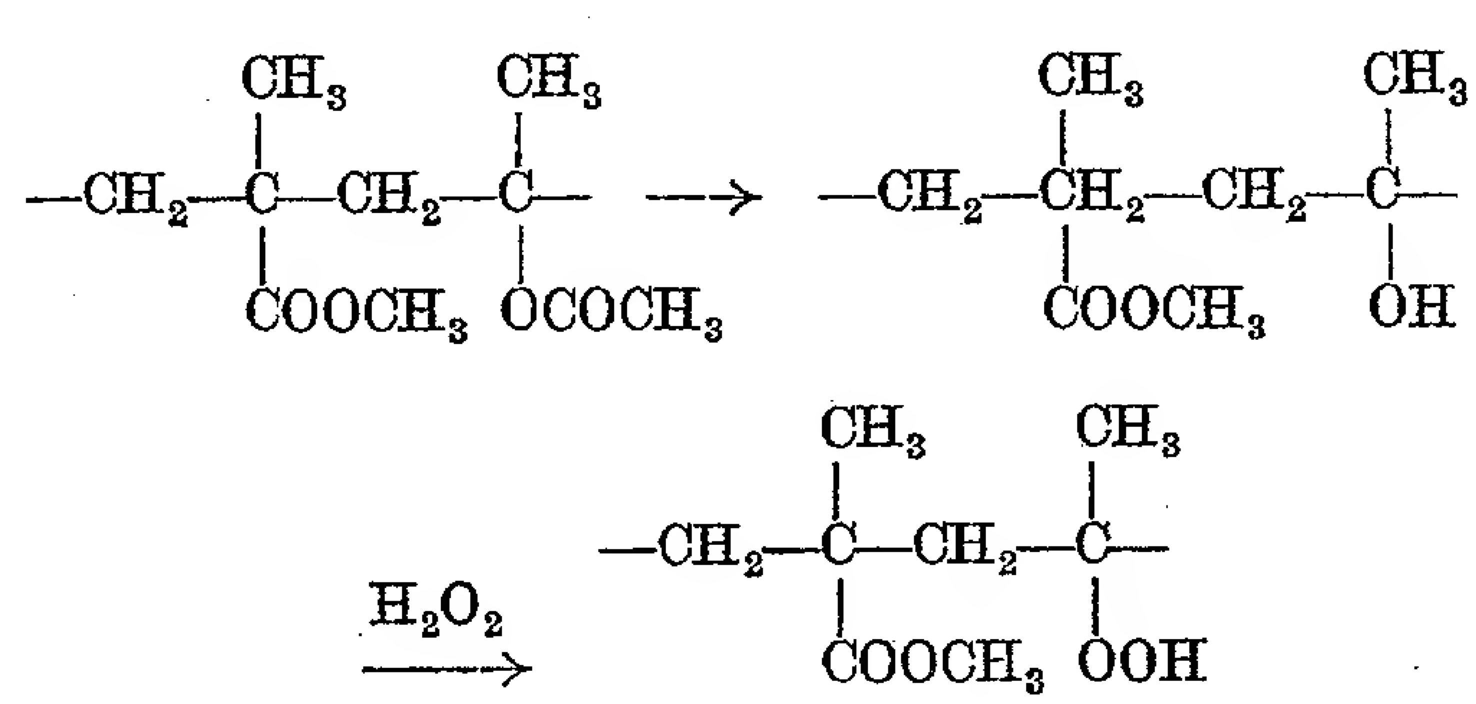
Several methods are known whereby epoxy groups may be introduced into polymeric materials and any of these methods may be employed to introduce peroxy groups into the normally solid high polymer to be used in the process of this invention.

A very convenient method of introducing peroxy groups is to subject the polymer to ionising radiation in the presence of oxygen or air. This method is applicable to a wide range of polymers and has the further advantage that it can be applied to polymers in shaped form. Suitable forms of ionising radiation include X-rays, γ-rays, β-rays, neutrons and accelerated electrons and heavy particles. These may be supplied from such sources as X-ray equipment, radioactive materials, atomic piles and electron accelerators. The type and amount of radiation employed will depend upon the number of peroxy groups it is desired to introduce into the polymer molecule. These groups act as active centres for the initiation of polymer chains in the production of the segmented polymer and their number determines the molecular configuration of the polymer. Thus, the closer the peroxy groups in the polymer, the greater will be the degree of branching in the segmented polymer. The number of peroxy groups introduced into the polymer molecule increases as the amount of ionising radiation employed is increased and it is necessary to determine empirically the amount of radiation from a particular source which is needed for the formation of the number of peroxy groups appropriate to the production of a desired segmented polymer.

Another method of introducing peroxy groups into polymers consists in subjecting the polymer to irradiation with ultra-violet light in the presence of air or oxygen.

Chemical methods may also be employed to introduce peroxy groups into polymers for use in the process of this invention. In one method, a small number of alkyl styrene units e.g. isopropyl- or isooctyl-styrene units, is incorporated in the molecule of the polymer by copolymerisation when the polymer is made. These units are then oxidised to peroxy units, a reaction which takes place readily under the influence of molecular oxygen.

Another chemical method consists in saponifying the isopropenyl acetate groups in a copolymer containing a small proportion of this monomer and then treating the saponified copolymer with hydrogen peroxide. The resulting reactions when a copolymer of methyl methacrylate and isopropenyl acetate is treated in this way may be represented as follows :—



Other known chemical methods of introducing peroxy groups into polymers include treating the polymers with sulphochromic acid, mixtures of sulphuric acid and potassium permanganate, aqua regia, Caro's acid or ozone.

Yet another method which may be employed for the introduction of peroxy groups into thermoplastic polymers consists in masticating the polymer in an oxygen-containing atmosphere at a temperature below 170° C. The mastication of the polymer may be carried out on an open-roll mill in the presence of atmospheric oxygen. It is preferred, however, to carry out the mastication in the presence of a concentration of oxygen greater than that normally present in the atmosphere. This may be achieved by directing a stream of oxygen on to the polymer as it is being milled. It is more convenient, however, to masticate the polymer in an enclosed chamber to which oxygen is supplied. It is therefore preferred to carry out the mastication in an enclosed internal mixer having a gas space to which oxygen is supplied or alternatively in an extruder into which oxygen is introduced either through a feed pipe directed into the hopper or through an inlet port in the barrel or screw which opens into the space between the barrel and the screw a short distance from the hopper in the direction in which the polymer moves through the extruder. The polymer is preferably masticated at a temperature at which the maximum shearing stress can be applied to the polymer by the masticating equipment used. When amorphous polymers are used this means that the temperature preferably lies between about 20° C. below the softening point of the polymer as determined by A.S.T.M. Heat Distortion Test D.648 and 170° C. On the other hand, when crystalline polymers, for example, polythene and polyvinylidene chloride, are used the preferred temperature range is from about 20° C. below the crystalline melting point of the polymer to either about 45° C. above the crystalline melting point or 170° C., whichever is the lower. In order that the temperature of the polymer may be suitably controlled during mastication the equipment used should be provided with efficient means for heating and/or cooling the material undergoing mastication.

It will be appreciated that the above methods of introducing peroxy groups into polymers are given by way of illustration only and that any other suitable method may also be used. It is possible for example to introduce peroxy groups into polythene simply by heating the polymer in an atmosphere of oxygen.

The polymer containing peroxy groups can if desired be irradiated with ultra-violet light in the presence of the monomeric compound immediately after its formation. Alternatively, it may if desired first be stored indefinitely at temperatures up to about 40° C.

Examples of monomeric compounds that may be used in the process of this invention include acrylic acid and esters thereof with saturated alcohols, e.g. methyl acrylate, ethyl acrylate, and *n*-butyl acrylate; substituted acrylic acids and esters thereof with saturated alcohols, e.g. methacrylic acid, methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, 2-ethoxy-ethyl methacrylate, and 2-chloro-ethyl methacrylate; nitriles and amides of acrylic and substituted acrylic acids, e.g. acrylonitrile, methacrylonitrile, acrylamide and *n*-butyl acrylamide; vinylidene compounds, e.g. vinylidene chloride and methyl isopropenyl ketone, vinyl compounds, e.g. vinyl chloride, styrene, substituted styrenes, e.g. vinyl toluenes and vinyl toluene sulphonic acids, vinyl acetate, methyl vinyl ketone, N-vinyl pyrrolidone, vinyl pyridines and vinyl carbazole; and compounds in which the olefinic double bond forms part of a ring structure, e.g. acenaphthalene. Monomeric compounds containing more than one olefinic double bond may also be used, including compounds containing conjugated olefinic double bonds, e.g. butadiene, isoprene, chloroprene and divinyl benzene, and compounds in which the olefinic double bonds are unconjugated, such as esters of acrylic acid and substituted acrylic acids with unsaturated alcohols or glycols, e.g. allyl acrylate, allyl methacrylate and ethylene dimethacrylate.

The monomeric compound may be used as such or in the form of a solution in an inert solvent.

It will be appreciated that if the polymer containing peroxy groups is one obtained by the free-radical polymerisation of a monomeric compound containing an olefinic double bond and this polymer is irradiated with ultra-violet light in the presence of the same monomeric compound as that from which it is derived, the product will be a segmented polymer of the homopolymeric type. If, on the other hand, the mixture irradiated contains a monomeric compound which polymerises to yield a polymer of dissimilar structure to the polymer containing peroxy groups, the product will be a segmented copolymer.

The ultra-violet light used in the process of this invention preferably has a wave-length within the range 2,000 and 5,000 Ångstrom units, wave-lengths of 2,800 to 3,800 Ångstrom units being particularly suitable. The particular wave-length used will depend however on the light transmitting characteristics of the walls of the vessel in which irradiation of the polymer/monomer mixture is carried out. For example, if the walls are made of ordinary soft glass, the

light transmitted is mainly that having a wave-length greater than 3,200 Ångstrom units. Light of lower wave-lengths may be used if the walls are made of silica.

The rate at which the peroxy groups in the polymer are decomposed by ultra-violet light is not influenced to any large extent by the temperature and it is usually convenient to carry out the irradiation at temperatures not far removed from room temperature. The use of low temperatures is particularly advantageous when the monomeric compound is gaseous since lower pressures are developed, thus making it possible to use simpler equipment.

Oxygen has a retarding effect on the polymerisation of many monomeric compounds. It is therefore in general desirable and in some cases essential to exclude oxygen during the irradiation of the mixture of polymer and monomeric compound e.g. by carrying out the irradiation in equipment which has previously been evacuated or flushed with an inert gas such as nitrogen or which is completely filled with the mixture being irradiated. The exclusion of oxygen need not be rigorous, e.g. it is not necessary to evacuate the polymer or monomeric compound and in some cases a rapid rate of polymerisation is possible without excluding oxygen. The necessity or desirability of excluding oxygen are also effected by other factors such as the absence or presence of polymerisation inhibitors in the polymer and monomeric compound e.g. if an inhibitor is present an added retarding effect due to oxygen may be more serious. Another factor is the solubility of oxygen in the polymer and in the monomeric material. In some cases, a low concentration of oxygen is found to be beneficial in that it increases the rate of polymerisation.

The present invention provides a convenient process for the production of segmented polymers which is of wide applicability. It is particularly valuable for the production of copolymers, since segmented copolymers are obtained which often exhibit a combination of properties not attainable by the copolymerisation of mixtures of monomeric compounds and are suitable for use in many diverse applications depending on the particular polymer and monomeric compound employed in their production.

Our invention is illustrated but not limited by the following examples.

Example 1.

600 g. of polythene granules, sold under the name " Alkathene " (Registered Trade Mark) Grade 2, were placed in a Baker-Perkins Size 3 Universal Heavy Duty Mixer and Masticator, and masticated for 30 minutes at 120° C. by rotating one rotor at 42 r.p.m. and the other at 49 r.p.m. whilst circulating a stream of oxygen through the mixer. A portion of the product was immersed in its own weight of styrene in a vessel made of silica and the mixture de-gassed by evacuation. The mixture was then irradiated for 2 hours with ultra-violet light from a high pressure mercury arc of 500 watts power, positioned at a distance of 10 cms. from the vessel containing the mixture. The main emission lines from this arc have a wave-length of 3,130 and 3,650 Å. At the end of the irradiation the mixture still contained some unpolymerised styrene. The mixture was extracted with boiling toluene and the part of the mixture insoluble after the toluene had cooled was isolated and dried. This insoluble part was found, on analysis, to contain 19% by weight of polymerised styrene which could not be separated from the polythene by solution techniques.

Example 2.

A sample of polythene, sold under the name " Alkathene " (Registered Trade Mark) Grade 2, which had been masticated in the presence of oxygen under conditions similar to those described in Example 1, was immersed in its own weight of acrylonitrile and irradiated with ultra-violet light for 2 hours under conditions similar to those described in Example 1. The resulting mixture was treated with dimethyl formamide to remove any acrylonitrile homopolymer. The insoluble part of the mixture was isolated and dried. It was found, on analysis, to contain 7% by weight of polymerised acrylonitrile.

Example 3.

Example 1 was repeated except that the monomer used was methyl methacrylate instead of styrene. The part of the product insoluble in cold toluene was found, on analysis, to contain 25% of polymerised methyl methacrylate which could not be separated from the polythene by solution techniques.

Example 4.

Polythene film was irradiated in an atmosphere of oxygen by high energy electrons from a 4 kv. linear accelerator until it had received a total dose of 5×10^5 rad. The irradiated film was placed in twice its own weight of methyl methacrylate in a silica vessel, de-gassed by evacuation and exposed for 2 hours to ultra-violet light from a high pressure mercury arc of 500 watts power, positioned at a distance of 10 cms. from the film. After extracting methyl methacrylate homopolymer with boiling toluene, the part of the product insoluble in cold toluene was found, on analysis, to contain 35% by weight of polymerised methyl methacrylate which could not be separated from the polythene by solution techniques.

EXAMPLE 5.

Polythene film was irradiated in an atmosphere of oxygen for 15 minutes with ultra-violet light from a high pressure mercury arc of 500 watts power, positioned at a distance of 10 cms. from the film. The irradiated film was immersed in its own weight of methyl methacrylate in a silica vessel, degassed by evacuation, and exposed again for 2 hours to ultra-violet light from the mercury arc at a distance of 10 cms. The product was extracted with boiling toluene and the part of the product insoluble after the toluene had cooled was isolated and dried. This insoluble part of the product was found, on analysis, to contain 20% by weight of polymerised methyl methacrylate which could not be separated from the polythene by solution techniques.

WHAT WE CLAIM IS :—

1. A process for the production of segmented polymers in which a normally solid high polymer having molecules containing peroxy groups is irradiated with ultra-violet light in the presence of a monomeric compound containing one or more olefinic double bonds and capable of polymerisation under the influence of free radicals, this irradiation being carried out in the absence of a concentration of oxygen which would otherwise inhibit polymerisation of said monomeric compound.

2. A process according to Claim 1 in which the ultra-violet light used has a wavelength within the range 2,000 to 5,000 Ångstrom units and preferably within the range 2,800 to 3,800 Ångstrom units.

3. A process according to either of the preceding claims in which the normally solid high polymer is polythene.

4. A process for the production of segmented polymers substantially as described hereinbefore with particular reference to the foregoing examples.

5. Segmented polymers whenever made by a process according to any of the preceding claims.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION.

Process for the Production of Polymeric Materials.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement :—

This invention relates to a process for the production of polymeric materials.

When the process of this invention is used for the production of copolymers, the products obtained are characterised by the presence in the molecule of long homopolymeric segments. Such copolymers are known as segmented copolymers. They may be of the type known as graft copolymers which consist of molecules having a backbone or skeleton of a polymer of one variety and side chains or branches of a different polymer and thus have a structure of the type

```
           B—B—B— . . . . .
           |
. . . . . —A—A—A—A—A—A— . . . . .
                  |
                  B—B—B— . . . . .
```

where A represents the monomeric unit of the polymer making up the backbone or skeleton of the copolymer and B represents the monomeric unit making up the side chains or branches. They may also be of the type known as block copolymers which have a structure of the type

. . . . —A—A—A—A—B—B—B—B— . . . .

Copolymers produced by the process of this invention may also have molecules in which both of these types of structure are present, i.e. they may be combinations of graft copolymers and block copolymers.

The process of this invention may also be used to modify the molecular structure of homopolymers. Thus a homopolymer having a substantially linear structure

. . . . . —A—A—A—A—A—A— . . . . .

may be converted into one having a branched structure of the type

```
             A—A—A— . . . . .
             |
. . . . . —A—A—A—A—A—A— . . . . .
                    |
                    A—A—A— . . . . .
```

In this way, it is possible to modify various properties, e.g. the solubility characteristics, of homopolymers.

In this Specification the expression segmented polymers is used as a generic term embracing both homopolymers having a branched structure of the type indicated above and also segmented copolymers.

According to the present invention we provide a process for the production of segmented polymers in which a normally solid high polymer having molecules containing

peroxy groups is irradiated with ultra-violet light in the presence of a monomeric compound containing an olefinic double bond and capable of polymerisation under the influence of free radicals, this irradiation being carried out in the absence of a concentration of oxygen which would otherwise inhibit polymerisation of said monomeric compound.

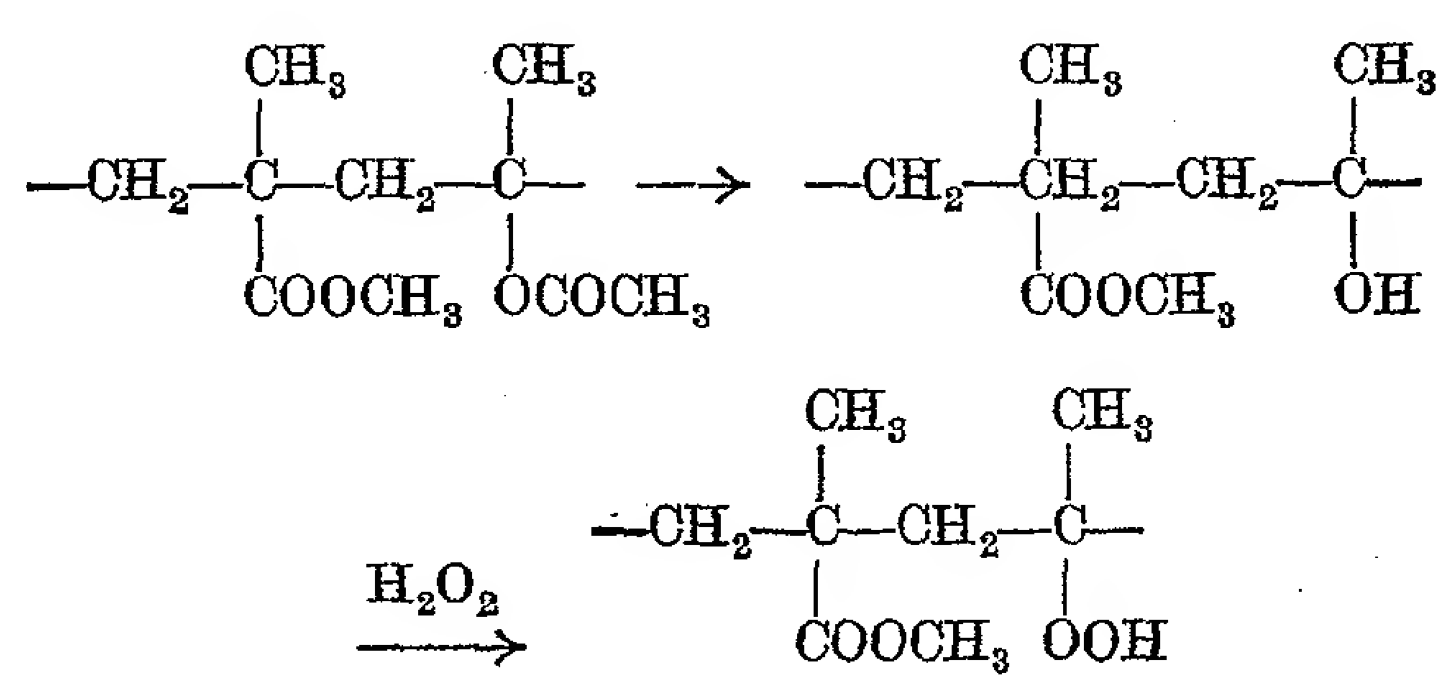
The normally solid high polymer used in the process of this invention may be of synthetic or natural origin. If a synthetic polymer is used, it may be of either the addition or condensation type. Examples of addition-type polymers include polythene, polypropylene, polyisobutylene, polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyvinyl formal, polyvinyl butyral, poly N-vinyl pyrollidone, polyvinyl pyridines, polyvinylidene chloride, polymethyl methacrylate, polybutyl methacrylate, polyacrylonitrile, polytrifluoromonochloroethylene, polytetrafluoroethylene, polybutadiene-1,3, polyisoprene and polychloroprene. Interpolymers and mixtures of polymers may also be used, e.g. interpolymers of butadiene 1,3 and styrene, acrylonitrile or methyl methacrylate. Examples of condensation-type polymers include epoxide polymers, polyethylene glycols, superpolyesters, superpolyamides, polyurethanes, polyureas and polysulphonamides. Examples of naturally occurring polymers include rubber, gutta percha, balata, cellulose, wool, cotton, silk, starch, casein, copal resins, shellac, and alginates. The invention is also applicable to modified naturally-occurring polymers e.g. to cellulose esters, ethers and acetals, cyclised natural rubber, rubber hydrochlorides and chlorinated rubber.

Several methods are known whereby peroxy groups may be introduced into polymeric materials and any of these methods may be employed to introduce peroxy groups into the normally solid high polymer to be used in the process of this invention.

A very convenient method of introducing peroxy groups is to subject the polymer to ionising radiation in the presence of oxygen or air. This method is applicable to a wide range of polymers and has the further advantage that it can be applied to polymers in shaped form. Suitable forms of ionising radiation include X-rays, γ-rays, β-rays, neutrons, and accelerated electrons and heavy particles. These may be supplied from such sources as X-ray equipment, radioactive materials, atomic piles and electron accelerators. The type and amount of radiation employed will depend upon the number of peroxy groups it is desired to introduce into the polymer molecule. These groups act as active centres for the initiation of polymer chains in the production of the segmented polymer and their number determines the molecular configuration of the polymer. Thus, the closer the peroxy groups in the polymer, the greater will be the degree of branching in the segmented polymer. The number of peroxy groups introduced into the polymer molecule increases as the amount of ionising radiation employed is increased and it is necessary to determine empirically the amount of radiation from a particular source which is needed for the formation of the number of peroxy groups appropriate to the production of a desired segmented polymer.

Chemical methods may also be employed to introduce peroxy groups into polymers for use in the process of this invention. In one method, a small number of alkyl styrene units e.g. isopropyl- or isooctyl-styrene units, is incorporated in the molecule of the polymer by copolymerisation when the polymer is made. These units are then oxidised to peroxy units, a reaction which takes place readily under the influence of molecular oxygen.

Another chemical method consists in saponifying the isopropenyl acetate groups in a copolymer containing a small proportion of this monomer and then treating the saponified copolymer with hydrogen peroxide. The resulting reactions when a copolymer of methyl methacrylate and isopropenyl acetate is treated in this way may be represented as follows—:



Other known chemical methods of introducing peroxy groups into polymers include treating the polymers with sulphochromic acid, mixtures of sulphuric acid and potassium permanganate, aqua regia, Caro's acid or ozone.

Yet another method which may be employed for the introduction of peroxy groups

into thermoplastic polymers consists in masticating the polymer in an oxygen-containing atmosphere at a temperature below 150° C. The mastication of the polymer may be carried out on an open-roll mill in the presence of atmospheric oxygen. It is preferred, however, to carry out the mastication in the presence of a concentration of oxygen greater than that normally present in the atmosphere. This may be achieved by directing a stream of oxygen on to the polymer as it is being milled. It is more convenient however, to masticate the polymer in an enclosed chamber to which oxygen is supplied. It is therefore preferred to carry out the mastication in an enclosed internal mixer having a gas space to which oxygen is supplied or alternatively in an extruder into which oxygen is introduced either through a feed pipe directed into the hopper or through an inlet port in the barrel or screw which opens into the space between the barrel and the screw a short distance from the hopper in the direction in which the polymer moves through the extruder. The polymer is preferably masticated at a temperature at which the maximum shearing stress can be applied to the polymer by the masticating equipment used. When amorphous polymers are used this means that the temperature preferably lies between about 60° C. below the softening point of the polymer as determined by A.S.T.M. Heat Distortion Test D.648 and either about 40° C. above this softening point or 150° C., whichever is the lower. On the other hand, when crystalline polymers, for example, polythene and polyvinylidene chloride, are used the preferred temperature range is from about 20° C. below the crystalline melting point of the polymer to either about 20° C. above the crystalline melting point or 150° C., whichever is the lower. In order that the temperature of the polymer may be suitably controlled during mastication the equipment used should be provided with efficient means for heating and/or cooling the material undergoing mastication.

It will be appreciated that the above methods of introducing peroxy groups into polymers are given by way of illustration only and that any other suitable method may also be used. It is possible for example to introduce peroxy groups into polythene simply by heating the polymer in an atmosphere of oxygen.

The polymer containing peroxy groups can if desired be irradiated with ultra-violet light in the presence of the monomeric compound immediately after its formation. Alternatively, it may if desired first be stored indefinitely at temperatures up to about 40° C.

Examples of monomeric compounds that may be used in the process of this invention include acrylic acid and esters thereof with saturated alcohols, e.g. methyl acrylate, ethyl acrylate, and *n*-butyl acrylate; substituted acrylic acids and esters thereof with saturated alcohols, e.g. methacrylic acid, methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, 2-ethoxy-ethyl methacrylate, and 2-chloro-ethyl methacrylate; nitriles and amides of acrylic and substituted acrylic acids, e.g. acrylonitrile, methacrylonitrile, acrylamide and *n*-butyl acrylamide; vinylidene compounds, e.g. vinylidene chloride, methyl isopropenyl ketone and isobutylene dimer ($C.(CH_3)_3—CH_2—C.(CH_3) = CH_2$); vinyl compounds, e.g. vinyl chloride, styrene, substituted styrenes, e.g. vinyl toluenes and vinyl toluene sulphonic acids, vinyl acetate, methyl vinyl ketone, N-vinyl pyrollidone, vinyl pyridines and vinyl carbazole; and compounds in which the olefinic double bond forms part of a ring structure, e.g. acenaphthalene and indene. Monomeric compounds containing more than one olefinic double bond may also be used, including compounds containing conjugated olefinic double bonds, e.g. butadiene, isoprene, chloroprene and divinyl benzene, and compounds in which the olefinic double bonds are unconjugated, such as esters of acrylic acid and substituted acrylic acids with unsaturated alcohols or glycols, e.g. allyl acrylate, allyl methacrylate and ethylene dimethacrylate.

The monomeric compound may be used as such or in the form of a solution in an inert solvent.

It will be appreciated that if the polymer containing peroxy groups is one obtained by the free-radical polymerisation of a monomeric compound containing an olefinic double bond and this polymer is irradiated with ultra-violet light in the presence of the same monomeric compound as that from which it is derived, the product will be a segmented polymer of the homopolymeric type. If, on the other hand, the mixture irradiated contains a monomeric compound which polymerises to yield a polymer of dissimilar structure to the polymer containing peroxy groups, the product will be a segmented copolymer.

The ultra-violet light used in the process of this invention preferably has a wave-length within the range 2,000 and 5,000 Ångstrom units, wave-lengths of 2,800 to 3,800 Ångstrom units being particularly suitable. The particular wave-length used will depend however on the light transmitting characteristics of the walls of the vessel in which irradiation of the polymer/monomer mixture is carried out. For example, if the walls are made of ordinary soft glass, the light transmitted is mainly that having a wave-length greater than 3,200 Ångstrom units. Light of lower wave-lengths may be used if the walls are made of silica.

The rate at which the peroxy groups in the

polymer are decomposed by ultra-violet light is not influenced to any large extent by the temperature and it is usually convenient to carry out the irradiation at temperatures not far removed from room temperature. The use of low temperature is particularly advantageous when the monomeric compound is gaseous since lower pressures are developed, thus making it possible to use simpler equipment.

Oxygen has a retarding effect on the polymerisation of many monomeric compounds. It is therefore in general desirable and in some cases essential to exclude oxygen during the irradiation of the mixture of polymer and monomeric compound e.g. by carrying out the irradiation in equipment which has previously been evacuated or flushed with an inert gas such as nitrogen or which is completely filled with the mixture being irradiated. The exclusion of oxygen need not be rigorous, e.g. it is not necessary to evacuate the polymer or monomeric compound and in some cases a rapid rate of polymerisation is possible without excluding oxygen. The necessity or desirability of excluding oxygen are also affected by other factors such as the absence or presence of polymerisation inhibitors in the polymer and monomeric compound e.g. if an inhibitor is present an added retarding effect due to oxygen may be more serious. Another factor is the solubility to oxygen in the polymer and in the monomeric material. In some cases, a low concentration of oxygen is found to be beneficial in that it increases the rate of polymerisation.

The present invention provides a convenient process for the production of segmented polymers which is of wide applicability. It is particularly valuable for the production of copolymers, since segmented copolymers are obtained which often exhibit a combination of properties not attainable by the copolymerisation of mixtures of monomeric compounds and are suitable for use in many diverse applications depending on the particular polymer and monomeric compound employed in their production.

ALFRED O. BALL,

Agent for the Applicants.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1960.
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